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**Name of Principal Investigators : Kopin Liu**

- e-mail address : kpliu@gate.sinica.edu.tw
- Institution : Institute of Atomic and Molecular Sciences
- Mailing Address : P.O. Box 23-166
- Phone : 886-02-2366-8259
- Fax : 886-02-2363-0578

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**Abstract:**

Exciting a stretching mode of a bond in a reactant should increase the likelihood of the bond breaking during a chemical reaction or, at the very least, have no impact on the reaction, according to conventional wisdom. A series of crossed molecular beam studies of the  $\text{Cl} + \text{CHD}_3/\text{CH}_4/\text{CH}_2\text{D}_2$  reactions, performed at IAMS, confirm this expectation. However, similar experiment on  $\text{F} + \text{CHD}_3$  has shown that, counter-intuitively, exciting the C-H bond effectively impedes its breakage to form  $\text{HF} + \text{CD}_3$ . The rate of the other possible reaction pathway - which leads to  $\text{DF}$  and  $\text{CHD}_2$  - also slows down. This unexpected finding was published in Science 325, 303 (2009) and has since received a wide publicity in C & E News, RSC Chemistry World, and Nature Chemistry.

**Introduction:**

The aim of this project is to understand and ultimately to control the reactive outcome of complex systems by vibrational excitations of a reactant. Reactions of methane with F, Cl, and O(3P) are of prototypical H-atom abstraction mechanism, yet with vastly different energetics and barrier properties. Hence, their contrasting behaviors upon vibrational and translational excitations can serve as benchmark for deeper insights into polyatomic reaction dynamics. Exploiting the product pair-correlation measurement enables us to elucidate the energy flow in the transition-state region, and to shed new light onto the mode- and bond-selective chemistry.

**Experiment:**

The crossed-beam experiment was performed using the rotating source machine at IAMS, which is equipped with a uniquely designed ion velocity map imaging detector capable of measuring the product pair correlation. The ultrafast femtosecond laser facility is housed in a newly constructed clean room. The installation and tests of the entire laser system is nearly complete, and some preliminary diagnostic experiments have just begun.

**Results and Discussion:**

We wrapped up the data analysis of the reactivity of Cl + stretch-excited methane. Being a competing reaction to  $\text{Cl} + \text{O}_3$  and one of the major sinks for  $\text{CH}_4$  (a greenhouse gas), this reaction plays a vital role in atmospheric chemistry and is highly relevant to the ozone-hole problems. Our aim is to understand how different forms of reagent energy (translation and vibration) affect the reaction rate and detail dynamics. Reactions of Cl-atom with different stretching-excited methane were chosen in this study:  $\text{CHD}_3(v_1=1$ ; the CH symmetric stretch),  $\text{CH}_4(v_3=1$ ; the CH anti-symmetric stretch), and  $\text{CH}_2\text{D}_2(v_1=1$  and  $v_6=1$ ) with  $v_1=1$  and  $v_6=1$  indicating one-quantum excitation of the  $\text{CH}_2$ -symmetric stretching and  $\text{CH}_2$ -antisymmetric stretching mode of the  $\text{CH}_2\text{D}_2$  reagent, respectively. Those stretching vibrations are nearly degenerate, but with distinct vibrational motions. The most important findings can be summarized as follows. (1) Compared to the respective ground-state reactions at the same initial collision energy, vibrational excitations of those modes all yield about the same enhancement factors. Yet, the observed vibrational enhancement is no more effective than an equivalent amount of translational

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energy. (2) The coincidentally formed  $\text{HCl}(v=1)$  fractions do not depend on the collisional energy for reactions with  $\text{CHD}_3(v_1=1)$  and  $\text{CH}_2\text{D}_2(v_1=1)$ , but display a fast decline as  $E_c$  increases for reactions with  $\text{CH}_4(v_3=1)$  and  $\text{CH}_2\text{D}_2(v_6=1)$ . This is the first clear experimental evidence that the reactant mode symmetry plays a vital role in governing the reaction dynamics, which will inspire theoretical studies.

A new series reaction of F-atom with methane has been performed. This is an early barrier reaction, namely the reaction barrier locates in the entrance valley of the potential energy surface. Exciting a stretching mode of a bond in a reactant should increase the likelihood of the bond breaking during a chemical reaction or, at the very least, have no impact on the reaction, according to conventional wisdom. Our findings are really astonishing, which showed that, counter-intuitively, exciting the C-H bond effectively impedes its breakage to form  $\text{HF} + \text{CD}_3$ . The rate of the other possible reaction pathway - which leads to  $\text{DF}$  and  $\text{CHD}_2$  - also slows down. This unexpected finding was published in *Science* 325, 303 (2009) and has since received a wide publicity in *C & E News*, *RSC Chemistry World*, and *Nature Chemistry*.

In the other project that is aimed to understand the hydration dynamics of aqueous solution, significant progresses have also been made. This is a new project funded by a very competitive 5-year Academia Sinica Investigator Award, starting from 2008. The major parts of a state-of-the-art femtosecond laser system have been purchased, installed and tested within a newly constructed clean-room unit. We also re-installed the water-cluster beam machine, equipped with a home-built retarding-field, time-of-flight mass spectrometer. The use of retarding field enables us to decipher the complicated fragmentation patterns of photoionized water clusters over two distinct time windows, 5 nsec - 1  $\mu$ sec and 1  $\mu$ sec - 10  $\mu$ sec. Some interesting yet puzzling results were observed and we are in the process of sorting them out. Attempts to add salt molecules to water clusters encountered many unexpected difficulties, thus we are back to the drawing board for alternative approaches. Meanwhile, we are also trying to dope  $\text{NO}_x$  to the water clusters to mimic the acid formation in the aqueous solution.

#### List of Publications:

##### SCI publications

1. "Uncovering a Spectrally Hidden REMPI band of  $\text{CD}_3$  by Ion Imaging Spectroscopy of the Products of the  $\text{Cl} + \text{CHD}_3(1_13_1)$  Reaction", J. Riedel and K. Liu, *J. Phys. Chem. A* (*G. C. Schatz Festschrift*) **113**, 4249-4254 (2009).
2. "Mode Specificity in Reactions of Cl with  $\text{CH}_2$  Stretch-Excited  $\text{CH}_2\text{D}_2(v_1, v_6 = 1)$ ", J. Riedel, S. Yan, and K. Liu, *J. Phys. Chem. A* (*V. Aquilanti Festschrift*) **113**, 14270-14276 (2009).
3. "IR-UV Double Resonance of Methyl Radicals and a Determination of the Detection Sensitivity of REMPI Bands", W. Zhang, H. Kawamata, A. J. Merer, and K. Liu, *J. Phys. Chem. A* (*R. W. Field Festschrift*) **113**, 13133-13138 (2009).
4. "CH Stretching Excitation in the Early Barrier  $\text{F} + \text{CHD}_3$  Reaction Inhibits CH Bond Cleavage", W. Zhang, H. Kawamata, and K. Liu, *Science* **325**, 303-306 (2009).
5. "Integral and Differential Cross Sections for the  $\text{S}(^1\text{D}) + \text{HD}$  Reaction Employing the Ground State Electronic State", H. Yang, K.-L. Han, G. C. Schatz, S. H. Lee, and K. Liu, *Phys. Chem. Chem. Phys.* **11**, 11587-11595 (2009).

##### Invited talks at Conferences (\* denoting plenary lectures)

- \*1. "The 13<sup>th</sup> East Asian Workshop on Chemical Reactions (EAWCR-13)", Taipei, Taiwan, March 17-21, 2009.
2. "Air Force Office of Scientific Research (AFOSR) Molecular Dynamics & Theoretical Chemistry Contractor's Meeting", San Diego, CA, May 17-19, 2009.
- \*3. "The 23<sup>rd</sup> International Symposium on Molecular Beams", Dalian, China, June 1-5, 2009.
4. "The 6<sup>th</sup> Biennial Conference of Overseas Chinese Physicists Association", Lanzou, China, Aug. 3-7, 2009.
- \*5. "XI National Chemical Dynamics Symposium", Yichang, China, Aug. 13-17, 2009.

##### Conference organized

"Asian International Symposium", in Annual meeting of the Chemical Society of Japan, Tokyo, Japan,

March 27-30, 2009.